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(54) **Method of insect control**

(57) A method of protecting a corn plant from destructive insects which comprises applying to the seed from which it grows or the soil from which the seed grows a composition comprising an insecticidal 1-arylpyrazole and an insect repellent. A composition comprising the insecticidal 1-arylpyrazole and the repellent.

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Description

[0001] The present invention relates to a new method of controlling destructive insects, a new composition and a product which comprises the composition.

[0002] It is known that 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole (fipronil) may be applied to corn seed at the time of planting to protect the said corn seed and the plants which emerge from the seed from *inter alia*, rootworms, e.g., *Diabrotica undecimpunctata howardi* and corn borers, e.g., *Ostrinia nubilalis*. In some cases, however, fipronil provides less than optimum activity against soil born pests, particularly against rootworms generally from the time of planting to the V6 growth stage of the corn plant.

[0003] It is also known to apply insecticidally effective amounts of pyrethroid insecticides at the time of planting to control certain pests, *inter alia*, rootworms, e.g., *Diabrotica undecimpunctata howardi*.

[0004] An object of the present invention is to provide an improved method of control of insects, particularly insects destructive to corn.

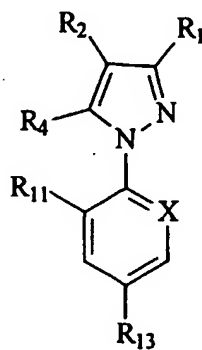
[0005] Another object of the present invention is to provide a long-lasting control of insects destructive to corn.

[0006] Another object of the present invention is to provide an improved method of using an insecticidal 1-arylpyrazole.

[0007] Another object of the present invention is to provide an improved method of using a pyrethroid insecticide.

[0008] These and other objects are met in whole or in part by the present invention.

[0009] The present invention provides a method of protecting a corn plant from destructive insects which method comprises applying to the seed from which it grows or the soil from which the seed grows an insecticidal 1-arylpyrazole and an insect repellent, which 1-arylpyrazole is a compound of formula (I):



(I)

wherein:

R₁ is CN or methyl;

R₂ is S(O)_nR₃;

R₃ is alkyl or haloalkyl;

R₄ is selected from the group consisting of a hydrogen atom, a halogen atom, and a radical which may be —NR₅R₆, —C(O)OR₇, —S(O)_mR₇, alkyl, haloalkyl, OR₈, or —N=C(R₉)(R₁₀);

R₅ and R₆ are independently selected from a hydrogen atom, alkyl, haloalkyl, —C(O)alkyl, —S(O)_iCF₃ and —C(O)OR₇; or R₅ and R₆ form together a divalent radical which may be interrupted by one or more heteroatoms, preferably selected from oxygen, nitrogen and sulphur;

R₄ is preferably an amino group, which is unsubstituted or which bears one or two substituents selected from the group consisting of alkyl, haloalkyl, acyl and alkoxycarbonyl;

R₇ is selected from alkyl and haloalkyl;

R₈ is selected from alkyl, haloalkyl and the hydrogen atom;

R₉ is selected from the hydrogen atom and alkyl;

R₁₀ is selected from phenyl and heteroaryl each of which is unsubstituted or substituted by one or more hydroxy, halogen, O-alkyl, —S-alkyl, cyano, or alkyl or combinations thereof;

X is selected from the nitrogen atom and the radical C-R₁₂;

R₁₁ and R₁₂ are independently selected from a halogen atom and the hydrogen atom;

R_{13} is selected from a halogen atom, haloalkyl, haloalkoxy, $S(O)_qCF_3$ and $-SF_5$, preferably from a halogen atom, haloalkyl, haloalkoxy, $-SF_5$;

m, n, q, r are independently selected from 0, 1 and 2;

provided that when R_1 is methyl, R_3 is haloalkyl, R_4 is NH_2 , R_{11} is Cl, R_{13} is CF_3 , and X is N. The 1-arylpyrazole and insect repellent are generally applied in a composition comprising them.

[0010] The alkyl and alkoxy groups of the formula (I) are preferably lower alkyl and alkoxy groups, that is, radicals having one to four carbon atoms. The haloalkyl and haloalkoxy groups likewise preferably have one to four carbon atoms. The haloalkyl and haloalkoxy groups can bear one or more halogen atoms; preferred groups of this type include $-CF_3$ and $-OCF_3$. It is to be understood that the ring formed by the divalent alkylene radical represented by R_5 and R_6 and including the nitrogen atom to which R_5 and R_6 are attached is generally a 5, 6, or 7-membered ring. When R_{10} is heteroaryl, it is preferably pyridyl, most preferably 2-pyridyl. It is to be understood that the 1-arylpyrazoles of formula (I) include enantiomers and/or diastereomers thereof.

[0011] The preparation of compounds of formula (I) can be effected according to any process described in International Patent Publications No. WO 87/03781, WO 93/06089 and WO 94/21606, as well as in European Patent Publication numbers 0295117, 0403300, 0385809 and 0679650, German Patent Publication 19511269 and United States Patents 5,232,940 and 5,236,938.

[0012] Preferably the compound of formula (I) has one or more of the following features:

R_1 is CN;

R_4 is $-NR_5R_6$;

R_5 and R_6 are independently selected from the hydrogen atom, alkyl, haloalkyl, $-C(O)alkyl$, $C(O)OR_7$;

X is C- R_{12} ; or

R_{13} is selected from a halogen atom, haloalkyl, haloalkoxy and SF_5 .

[0013] Most preferably the compound of formula (I) is 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethyl(phenyl)-4-trifluoromethylsulfinylpyrazole (i.e. fipronil) or 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-ethylsulfinylpyrazole hereinafter known as Compound B.

[0014] In a preferred embodiment, the repellent is applied in a substantially non-lethal amount. By the term "substantially non-lethal" is meant an amount, which when delivered to the soil alone kills less than 10% of the pests so-controlled by the method of the invention. Preferably the repellent kills less than 5% of the pests.

[0015] The repellent may be a known insect repellent. Preferably the insect repellent is a pyrethroid insecticide. Preferably, the repellent is a pyrethroid insecticide that is selected from the group consisting of tefluthrin, permethrin, fenvalerate, esfenvalerate, cypermethrin, cyhalothrin, lambda-cyhalothrin, bifenthrin and deltamethrin.

[0016] Generally the pests controlled by the method include *Agrotis spp.*, e.g. Black cutworm, rootworms, including *Diabrotica spp.*, e.g. *Diabrotica undecimpunctata howardi* or *Diabrotica virgifera*; or corn seed maggot, e.g. *Hylemya platura*, *Chortophila platura*, *Chortophila cilicrura*, *Hylemya cilicrura*, *Phorbia platura*, *Chortophila funesta*, *Chortophila fusciceps*, *Crinura cilicrura*, *Crinura platura*, *Crinura fusciceps*, *Crinura funesta*, *Delia cilicrura*, *Delia funesta*, *Delia fusciceps*, *Hylemya funesta*, *Hylemya fusciceps*, *Phorbia cilicrura*, *Phorbia funesta*, *Phorbia fusciceps*, *Hylemya cana*, *Delia cana*, *Hylemya cana*, or *Delia platura*.

[0017] Generally, the weight to weight ratio of the insecticidal 1-arylpyrazole to the repellent is from 2:1 to 200:1, preferably from 5:1 to 75:1, most preferably from 8:1 to 50:1.

[0018] The composition is generally applied as a liquid composition to the soil or as a seed treatment to the seed from which the corn plant grows.

[0019] In a highly preferred embodiment, the liquid composition may be directed into the soil mixing zone below the level of the top of a furrow in which the corn seed may be planted. In this way, the composition may be incorporated in the soil below the level of the soil, on the seed and above the seed as the furrow is closed. The application spray can be a stream of liquid or a conical spray.

[0020] Generally, the volume of liquid to be used per unit land area is from 0.1 to 50 gallons per acre (0.9 to 470 L/ha), preferably from 0.2 to 10 gal/A (1.9-90 L/ha), more preferably from 0.5 to 5 gal/A (4.7 — 47 L/ha), most preferably from 1 to 3 gal/A (9.4—28 L/ha).

[0021] When the repellent is a pyrethroid insecticide, it is preferably used at about 1% to 90% of the labelled insecticidal use rate, preferably from 5% to 50%. The following table provides a general guidance to preferred rates to be used in the method of the present invention.

Repellent	Current Field Use Rate in Corn (lb.ai/acre)	Use rate according to the present invention (lb. ai/acre)
tefluthrin	0.075 - 0.15	0.001 - 0.02
esfenvalerate	0.03 - 0.05	0.001 - 0.02
lambda-cyhalothrin	0.015 - 0.030	0.001 - 0.01
permethrin	0.1 - 0.2	0.01 - 0.02
cyfluthrin	not labelled	0.001 - 0.05

[0022] The abbreviation "ai" means active ingredient.

[0023] The rate of use of the 1-arylpyrazole is generally from 0.01 lb. per acre (11 g per hectare) to about 2.2 lb./acre (1000 g/Ha), preferably from 20 to 200 g/Ha.

[0024] In a highly preferred embodiment of the invention, the composition is applied when the soil temperature is from 4°C to 25°C, preferably from 10°C to 20°C. In this way there is a better insecticidal effect on the above insect species than with the 1-arylpyrazole insecticide alone.

[0025] The present invention also provides an agriculturally acceptable composition for protecting corn plants from destructive insects which comprises an insecticidal 1-arylpyrazole as defined above and a repellent, preferably a substantially non-lethal amount of an insect repellent as defined above. The composition may be, for example, a liquid composition or a granular composition, preferably a liquid composition in use. Liquid compositions include those known to the skilled addressee and emulsifiable concentrates, suspension concentrates or aqueous emulsions are generally preferred.

[0026] The present invention also provides a product comprising an insecticidal 1-arylpyrazole as defined above and a repellent for simultaneous, separate or sequential use in the control of destructive insects of corn on or on the soil from which the corn grows. Preferably the product may be a premixed product which comprises both the 1-arylpyrazole and the repellent.

[0027] The following non-limiting example illustrates the invention:

Example 1:

[0028] Corn seed is planted in a field where the average temperature of the soil is about 10°C. As the corn seed is planted, fipronil (as the commercial product Regent® 80WG) and lambda-cyhalothrin (as the commercial product Warrior®) are applied simultaneously on the seed as a liquid composition in water at rates of 0.13 lbs/acre (0.15 kg/Ha) and 0.01 lbs/acre (0.011 kg/Ha) respectively. One part of the field is treated with Regent 80WG at 0.13 lbs./acre alone. After 4 weeks, several plants are removed to determine the damage to the roots and stalks. The treatment with fipronil and lambda-cyhalothrin provides a lower numerical Iowa Root rating than the treatment with Regent alone. There is less damage from black cutworm in the fipronil + lambda cyhalothrin treatment than in the fipronil treatment.

Example 2:

[0029] The procedure of Example 1 is used with fipronil (as the commercial product Regent® 4SC) and Cyfluthrin (as the commercial product Baythroid®) at rates of 0.13 lbs/acre (0.15 kg/ha) and 2.6 ounces product/acre (0.023 kg/ha). One part of the field is treated with Regent® 4SC at 0.13 lbs/acre (0.15 kg/ha) alone and another part of the field is treated with Baythroid® at 2.6 ounces product/acre (0.023 kg/ha) alone.

[0030] Toward the end of the growing season, the plants are removed to determine damage to the roots. The following results are observed.

TREATMENT	IOWA ROOT RATING
Regent 4SC	3.4

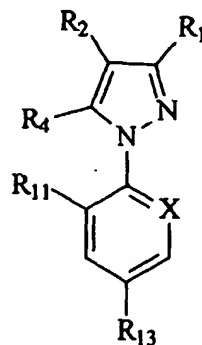
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TREATMENT	IOWA ROOT RATING
Baythroid	4.2
Regent + Baythroid	2.6

[0031] While the invention has been described in terms of various preferred embodiments, the skilled artisan will appreciate that various modifications, substitutions, omissions, and changes may be made without departing from the spirit thereof. Accordingly, it is intended that the scope of the present invention be limited solely by the scope of the following claims, including equivalents thereof.

Claims

1. A method of protecting a corn plant from destructive insects which method comprises applying to the seed from which it grows or the soil from which the seed grows an insecticidal 1-arylpyrazole and an insect repellent, which 1-arylpyrazole is a compound of formula (I):



(I)

wherein:

R₁ is CN or methyl;

R₂ is S(O)_nR₃;

R₃ is alkyl or haloalkyl;

R₄ is selected from the group consisting of a hydrogen atom, a halogen atom, and a radical which may be —NR₅R₆, —C(O)OR₇, —S(O)_mR₇, alkyl, haloalkyl, or OR₈, or —N=C(R₉)(R₁₀);

R₅ and R₆ are independently selected from a hydrogen atom, alkyl, haloalkyl, —C(O)alkyl, —S(O)_rCF₃ and —C(O)OR₇; or R₅ and R₆ form together a divalent radical which may be interrupted by one or more heteroatoms;

R₄ is preferably an amino group, which is unsubstituted or which bears one or two substituents selected from the group consisting of alkyl, haloalkyl, acyl and alkoxy carbonyl;

R₇ is selected from alkyl and haloalkyl;

R₈ is selected from alkyl, haloalkyl and the hydrogen atom;

R₉ is selected from the hydrogen atom and alkyl;

R₁₀ is selected from phenyl and heteroaryl each of which is unsubstituted or substituted by one or more hydroxy, halogen, O-alkyl, —S-alkyl, cyano, or alkyl or combinations thereof;

X is selected from the nitrogen atom and the radical C—R₁₂;

R₁₁ and R₁₂ are independently selected from a halogen atom and the hydrogen atom;

R₁₃ is selected from a halogen atom, haloalkyl, haloalkoxy, S(O)_qCF₃ and —SF₅, preferably from a halogen atom, haloalkyl, haloalkoxy, —SF₅;

m, n, q, r are independently selected from 0, 1 and 2;

provided that when R_1 is methyl, R_3 is haloalkyl, R_4 is NH_2 , R_{11} is Cl, R_{13} is CF_3 , and X is N.

2. The method according to claim 1 wherein the repellent is an insecticide applied in a substantially non-lethal amount.
3. The method according to claim 1 or claim 2 wherein the repellent is a pyrethroid insecticide.
4. The method according to claim 3 wherein the repellent is a pyrethroid insecticide which is selected from the group consisting of tefluthrin, permethrin, fenvalerate, esfenvalerate, cypermethrin, cyhalothrin, lambda-cyhalothrin, bifenthrin and deltamethrin.
5. The method according to any one of the foregoing claims wherein the insect is *Agrotis spp.*, preferably black cutworm; a rootworm, preferably *Diabrotica spp.*, more preferably *Diabrotica undecimpunctata howardi* or *Diabrotica virgifera*; or corn seed maggot, preferably *Hylemya platura*, *Chortophila platura*, *Chortophila cilicrura*, *Hylemya cilicrura*, *Phorbia platura*, *Chortophila funesta*, *Chortophila fusciceps*, *Crinura cilicrura*, *Crinura platura*, *Crinura fusciceps*, *Crinura funesta*, *Delia cilicrura*, *Delia funesta*, *Delia fusciceps*, *Hylemya funesata*, *Hylemya fusciceps*, *Phorbia cilicrura*, *Phorbia funesta*, *Phorbia fusciceps*, *Hylemya cana*, *Delia cana*, *Hylemya cana*, or *Delia platura*.
6. The method according to any one of the foregoing claims wherein the 1-arylpyrazole has one or more of the following features:
 - R_1 is CN;
 - R_4 is $-NR_5R_6$;
 - R_5 and R_6 are independently selected from the hydrogen atom, alkyl, haloalkyl, $-C(O)alkyl$, $C(O)OR_7$;
 - X is C- R_{12} ; or
 - R_{13} is selected from a halogen atom, haloalkyl, haloalkoxy and $-SF_5$.
7. The method according to any one of the foregoing claims wherein the insecticidal 1-arylpyrazole is 5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-trifluoromethylsulfinylpyrazole.
8. The method according to any one of the foregoing claims wherein the weight to weight ratio of the insecticidal 1-arylpyrazole to the repellent is from 2:1 to 200:1, preferably from 5:1 to 75:1, most preferably from 8:1 to 50:1.
9. The method according to any one of the foregoing claims wherein the composition is applied when the soil temperature is from 4°C to 25°C, preferably from 10° to 20°C.
10. The method according to any one of the foregoing claims wherein the insecticidal 1-arylpyrazole is applied at a rate of from 11 grams per hectare to about 1000 gha.
11. An agriculturally acceptable composition for protecting corn plants from destructive insects which comprises an insecticidal 1-arylpyrazole as defined in any one of the foregoing claims and an insect repellent as defined in any one of the foregoing claims, in association with an agriculturally acceptable carrier.
12. A product comprising an insecticidal 1-arylpyrazole as defined in any one of the foregoing claims and an insect repellent as defined in any one of the foregoing claims for simultaneous, separate or sequential use in the control of destructive insects of corn in or on the soil from which the corn grows.
13. The product of claim 12 which is a premixed package of the insecticidal 1-arylpyrazole and the repellent.



European Patent
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EUROPEAN SEARCH REPORT

Application Number
EP 98 31 0583

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	WO 95 22902 A (RHONE-POULENC AGROCHIMIE ; KODAMA HIROSHI (JP); WADA YASUHIRO (JP);) 31 August 1995	11-13	A01N43/56 A01N53/00 //(A01N43/56, 53:00)
Y	* page 4, line 5-18; examples 1-3; table 1 *	1-10	
X	US 5 516 787 A (TAKADA YOJI) 14 May 1996	11-13	
Y	* column 2, line 43-56 *	1-10	
D,Y	WO 93 06089 A (ICI PLC) 1 April 1993 * page 8, paragraph 3-6 *	1-10	
Y	C. D. S. TOMLIN (ED.): "The Pesticide Manual" 1997, BRITISH CROP PROTECTION COUNCIL, FARNHAM XP002103044 page 545 - 547: Fipronil: 'Applications'.	1-10	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			A01N
The present search report has been drawn up for all claims			
Place of search MUNICH		Date of completion of the search 18 May 1999	Examiner Klaver, J
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EPO FORM 1500 (03/92) (P04001)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 98 31 0583

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
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18-05-1999

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9522902	A	31-08-1995	AU 679622 B	03-07-1997
			AU 1810495 A	11-09-1995
			BR 9507118 A	12-08-1997
			CA 2183341 A	31-08-1995
			CN 1141580 A	29-01-1997
			EP 0746205 A	11-12-1996
			JP 7285813 A	31-10-1995
			US 5747519 A	05-05-1998
			ZA 9501611 A	07-12-1995
US 5516787	A	14-05-1996	JP 7173021 A	11-07-1995
			BR 9405163 A	17-10-1995
			CN 1106993 A	23-08-1995
			ES 2108619 A	16-12-1997
			FR 2713891 A	23-06-1995
			IT T0941036 A	20-06-1995
			US 5629334 A	13-05-1997
WO 9306089	A	01-04-1993	AT 163180 T	15-02-1998
			AU 664199 B	09-11-1995
			AU 2541392 A	27-04-1993
			AU 692902 B	18-06-1998
			AU 3051295 A	23-11-1995
			BR 9206552 A	17-10-1995
			CA 2119385 A	01-04-1993
			CN 1071163 A, B	21-04-1993
			CN 1115205 A	24-01-1996
			CZ 9400712 A	13-07-1994
			DE 69224437 D	19-03-1998
			DE 69224437 T	04-06-1998
			EP 0605469 A	13-07-1994
			ES 2112913 T	16-04-1998
			GR 3026099 T	29-05-1998
			HU 66735 A, B	28-12-1994
			JP 7500319 T	12-01-1995
			MX 9205468 A	01-03-1993
			NZ 244265 A	28-03-1995
			TR 26511 A	15-03-1995
			US 5451598 A	19-09-1995
			ZA 9206785 A	09-06-1993

EPO FORM P0139

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82